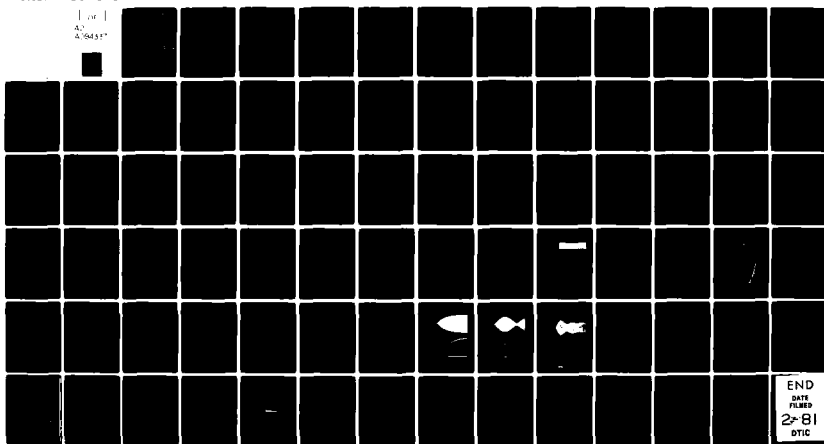


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Rochester, New York 14627

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The possibility of controlling surface phenomena and heterogeneous catalysis by means of laser radiation is finally presented in the framework of the theoretical modellings. Greater details of the theoretical works and some suggested experimental measurements of LSSP are included in the Appendices.

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LASER-STIMULATED SURFACE PROCESSES
AND HETEROGENEOUS CATALYSIS

by

Jui-teng Lin

Submitted in Partial Fulfillment
of the
Requirements for the Degree
Doctor of Philosophy

Supervised by Professor Thomas F. George
Department of Chemistry

University of Rochester
Rochester, New York

1980

In memory of my mother 美 and father 金山

VITAE

The author was born on May 5, 1948, in Taiwan, Republic of China. He received his B.S. Degree in Physics from National Taiwan Normal University in 1971. After one year's teaching in Puli High School (1971-72), he attended the Institute of Physics, Tsin Hua University (Taiwan) and received his Master Degree in Solid State Physics in 1974. Then he served in the Chinese Army Signal School as an instructor from May, 1974 to May, 1976.

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1. J. Lin, *A Classical Model for Stochastic Multiphoton Absorption Processes of Anharmonic Molecules*, Phys. Lett. A70, 195 (1979).
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ABSTRACT

A theoretical study of laser-stimulated surface processes (LSSP), motivated by potentialities in the areas of chemical technology, materials science and academic research, is presented. The possibility of the new phenomena of laser-controlled surface processes (migration, recombination, desorption and heterogeneous rate processes) is demonstrated within the framework of model systems. The purpose of this work is twofold: (1) To create a theoretical foundation for an understanding of the quantitative and semi-quantitative aspects of LSSP, and (2) To provide possible mechanisms and suggest relevant measurements of LSSP with applications to laser-activated rate processes.

To help lay the foundation for studies of LSSP, simple classical models are first presented for the multiphoton absorption (MPA) processes of a homogeneous system (e.g., SF_6). It is shown that the excitation and relaxation dynamical nature of MPA may be characterized by the calculated absorption cross section (or line shape), which is governed by the memory effects of the bath-induced energy (T_1) and phase (T_2) relaxation and the nonlinearity due to the anharmonicity.

For a heterogeneous system of LSSP, the major features and the dynamical behavior are studied by both classical and quantum models, where each model provides some mechanism for the processes. They include: (i) microscopic model Hamiltonians (in the Heisenberg-Markovian picture) of multiphoton-multiphonon processes; (ii) quantum dynamical model (in the Schrodinger picture) for the selective vs nonselective nature of LSSP; (iii) Pauli master equations in photon-energy space for the energy distributions and associated desorption probabilities of the adspecies (both the thermal Boltzmann and the nonthermal Poisson-type distribution are presented); (iv) phenomenological classical models for the average power absorption of the system, where the many-body effects of the surface atoms are replaced by the damping factor and the frequency-shift; (v) the generalized Langevin theory for the dynamical behavior of LSSP by including the memory effects of the damping and dephasing kernel and the interaction between the active modes; (vi) coupled Newton's equations of a model CO/Ni adspecies/surface system for the numerical simulation of the atom amplitudes and the energies stored in the bonds; and (vii) semiclassical model for the laser-selective nature via the multiphonon coupling strength and the "internal resonant" condition.

The possibility of controlling surface phenomena and heterogeneous catalysis by means of laser radiation is

finally presented in the framework of the theoretical modelings. The greater details of the theoretical works and some suggested experimental measurements of LSSP are included in the Appendices.

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GLOSSARY OF ACRONYMS

CTRW	-	Continuous Time Random Walk
CVD	-	Chemical Vapor Deposition
ETD	-	Effective Thermal Desorption
GME	-	Generalized Master Equation
GLE	-	Generalized Langevin Equation
HMP	-	Heisenberg-Markovian Picture
IVR	-	Intramolecular Vibrational Relaxation
LEED	-	Low-Energy Electron Diffraction
LHC1	-	Local Heating of C_1 modes
LSD	-	Laser-Selective Desorption
LSSP	-	Laser-Stimulated Surface Processes
LSGLE	-	Laser-Stimulated Generalized Langmuir Equation
MPA	-	Multiphoton Absorption
MPD	-	Multiphoton Dissociation
NSE	-	Nonselective Excitation
RWA	-	Rotating Wave Approximation
SEA	-	Selective Excitation of Active Mode
SEB	-	Selective Excitation of Bath Modes
VLSI	-	Very Large Scale Integrated Circuits

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CHAPTER I

INTRODUCTION

1.1 General Introduction

The phenomena of the laser (light amplification by stimulated emission of radiation), discovered in the early 1960's, has become one of the most exciting developments in science. The laser, providing a source of intense, coherent and monochromatic radiation, has already had a remarkable effect on research in many areas of physical, chemical and biological sciences. In recent years, a considerable amount of research activity has been directed toward understanding the phenomena of the interactions of photons with matter (in the gas phase, condensed phase and gas/surface mixed phase) both experimentally and theoretically.¹⁻¹⁶

In the general area of laser chemistry and quantum electronics, multiphoton ionization (MPI) of atoms and multiphoton dissociation (MPD) of molecules represent some of the most timely and exciting phenomena.¹⁵ One of the most widely studied subjects is the infrared MPD of SF_6 , which was among the first molecules to be dissociated by a high-power CO_2 laser. Certain aspects of MPD, such as frequency response, isotope separation factors and laser

coherence effects, have been investigated and provide descriptions of the excitation mechanism, e.g., the intensity and energy fluence dependent excitations in different stages of the excited molecule, the possible role of energy localization in selective bonds and the dissociation dynamics.^{13,14} Multiphoton absorption processes of homogeneous (gas-phase) systems have stimulated great interest in many different areas because of promising applications such as isotope separation, laser-induced chemical decomposition, laser-enhanced reaction rates, gas purification and development of chemical lasers.

While the interaction of lasers with matter in the gas phase has been extensively studied, the influence lasers on heterogeneous gas/surface systems, which is the essential ingredient of catalysis, has only recently been studied.^{3-12,15,16} The studies of this novel field of laser-stimulated surface processes (LSSP) have been motivated by its potential importance not only in the area of academic research but also in chemical technology (e.g., laser-induced chemical vapor deposition, laser-enhanced heterogeneous catalysis and laser-assisted fabrication of very-large scale integrated circuits), materials science (e.g., laser annealing and laser micromachining)¹⁷ and medical science (e.g., laser prevention of dental caries).¹⁸ Recent experimental evidence has shown that the effects of laser radiation on surface rate processes can be nonthermal in nature, involving the laser radiation and the catalyst surface

in a resonant, synergistic process.¹⁶ The interaction of a laser with a heterogeneous (gas/surface) system is characterized not only by the frequency, intensity and coherent feature of the laser field but also by the structure of the surface, the adsorption state and the dynamical behavior of the excited species on the surface (migration, diffusion and desorption). Depending on the frequencies of the laser radiation (UV, visible or IR), the heterogeneous system may be electronically, rotationally and/or vibrational excited with the consequent processes of ionization, migration, dissociation or desorption. When the photon energy is absorbed by the optically active mode(s) of the system with subsequent relaxation to the bath modes, the intramolecular and intermolecular couplings play an essential role in the pattern of the photon energy distribution, i.e., the selective versus nonselective nature of LSSP.^{8,9}

In probing surface phenomena, many new methods have been used recently, e.g., LEED (low-energy electron diffraction), SEXAFS (surface-extended X-ray absorption fine structure), ARPES (angular-resolved photoelectron spectroscopy), SERS (surface-enhanced Raman spectroscopy) and LSSP (laser-stimulated surface processes). These methods provide one or several components of the information about the following features: the reconstruction of the surface, the spacing of the surface layer, the positions and masses of the surface atoms, the bond length and orientation of the adspecies and the catalytic mechanism of the surface.¹⁹ We note that the method of LSSP,

while providing the heterogeneity feature of the gas/surface system, is particularly powerful in the study of the dynamical behavior of surface processes (diffusion, migration, desorption, decomposition and recombination rate processes).³ Therefore, a full understanding of LSSP involves inter-disciplinary research in the fields of physics, chemistry, solid-state science and optics. Motivated by the academic and industrial potential of LSSP, this thesis work will provide a theoretical foundation for an understanding of the quantitative and semi-quantitative aspects of this novel area as well as proposed possible mechanisms to interpret the experimental evidence. The thesis is outlined as follows.

In Chapter I, which serves as the introduction to this thesis, the current understanding and the fundamental mechanism of MPA and LSSP are presented by posing the related questions which essentially characterize the dynamical nature of the interaction of laser photons with matter. While the main focus of this thesis is on LSSP in heterogeneous systems, the methodology of MPA for a homogeneous system (e.g., SF_6) is discussed first, since the techniques developed for MPA help form a basis for studies of LSSP. The methodology of LSSP, including classical and quantum models, microscopic and phenomenological methods, numerical and analytical approaches, is presented systematically with the intercorrelation between them.

The details of the accomplished research begin with Chapter II. Some major features of MPA are studied by means of calculated absorption cross sections, which

reflect not only the internal level structure of a system but also the dynamical behavior of the various processes. A simple anharmonic model and a generalized Langevin theory, with the memory effects of the damping and dephasing kernel and the nature of the laser-selective effects, are presented.

In Chapter III, the important results of LSSP and the possibility of laser-controlled surface phenomena and heterogeneous catalysis are discussed. The model systems characterizing various processes of LSSP are described by: (i) microscopic model Hamiltonians #1 and #2 for multiphoton-multiphonon processes and laser-stimulated surface migration, respectively; (ii) quantum dynamical model (in the Schrödinger picture) for the selective vs nonselective nature of LSSP; (iii) Pauli master equation in photon-energy space for the energy populations and desorption probabilities; (iv) phenomenological models (classical anharmonic model and the generalized Langevin stochastic model) for the temperature-dependent power absorption and the dynamical behavior of LSSP; and (v) numerical simulation of coupled Newton's equations for the amplitudes and the energies stored in different bonds of a five-atom linear chain representing the CO/Ni adspecies/surface system. More extensive details of this work are contained in the Appendices (which are Publications #1-12 listed on pages iv and v).

1.2 Fundamental Mechanism of MPA

The well-accepted feature of multiphoton absorption (MPA) and dissociation (MPD) are viewed in terms of three different energy regions (see Fig.1): I. low-vibrational energy region where the molecular levels are sparse, and the excitation involves near-resonant absorption of several IR photons described by the coherent Bloch equation model;²⁰ II. higher-vibrational energy region where the high density of states forms a quasicontinuum; and III. the reaction region where the molecules acquire enough energy to dissociate. In regions II and III, the excitation processes are incoherent with all phase memory lost, and rate equation models are found to fit much of the experimental data.²¹

The dynamical features of MPA governed by the following fundamental mechanisms have been studied in this thesis:

- 1) How is the absorption cross section of the system affected by the transition nature of MPA (i.e., from coherent to incoherent excitation)?

- 2) How can a general line shape function reflect the absorption dynamics and the internal level structure of MPA via the memory effects of the damping and dephasing kernel and the rate of intramolecular vibrational relaxation (IVR)?

- 3) How does the IVR rate play an important role in selective bond breaking, and what is the requirement for a slow IVR rate via multiquantum exchange processes?

Figure 1. Schematic representation of the discrete, quasi-continuous and dissociation regions of the energy level diagrams of a polyatomic molecule.

In this thesis, three models are presented to describe the above features of MPA: (1) classical anharmonic model with a stochastic driving field; (2) generalized Langevin dynamical model with memory effects; and (3) quantum model governed by the multiquantum coupling strength and the "internal resonant" condition.

1.3 Fundamental Mechanism of LSSP and Heterogeneous Catalysis

Some potential areas of the applications of LSSP are:^{5,7}

- 1) Enhancement of surface diffusion-limited reactions.
- 2) Enhancement of the mobilities of selective species in a multicomponent environment.
- 3) Control of the surface concentration of the reagents of rate processes via selective desorption or excitation-induced migration of the adspecies.
- 4) Study of decomposition and recombination rate processes on a solid surface.
- 5) Study of catalytic properties and heterogeneity features of the adsorbent surface via the composition and location of the active centers.
- 6) Study of the resolution, purification and growth rate of a deposited film via the laser-assisted chemical vapor deposition (CVD).

The above laser-stimulated surface phenomena (migration, desorption, recombination, deposition and rate processes) center on the fundamental mechanisms of: how the radiative pumped mode(s) of the system absorbs energy from the laser field and relaxes to its environment, how the laser radiation affects the dynamical behavior of the adspecies, and what is the deposition pattern of the photon energy absorbed by the heterogeneous system. The main stages of heterogeneous catalysis, by current understanding, involve:²² (1) adsorption

of the adspecies, (2) formation of the unstable complexes on the catalytic surface, (3) dissociation (or decomposition) of these complexes and (4) desorption of the reaction products. [Some prototypes of surface-catalyzed rate processes are referred to in Ref.16.]

The effects of laser-radiation on the catalytic rate processes depend not only upon the nature of the solid surface (metal, insulator or semiconductor), the heterogeneity of the adsorbate (physisorption or chemisorption, dissociative or associative),^{3,22} and the electronic and vibrational structures of the adspecies/surface system (or the density of states in the frequency domain), but also upon the nature of the laser field (intensity, frequency, polarization and the angle of incidence of the field).^{7,8} Thus, a complete understanding of LSSP and its application in heterogeneous catalysis, governed by a series of physical and chemical processes, requires a rigorous, quantitative description of the dynamics involved.

The intention of the thesis work has not been to provide a complete, quantitative theoretical basis for LSSP (a rather formidable task!). Rather, it has been to create a theoretical foundation for an understanding of the qualitative and semiquantitative aspects of this novel area of research. While part of the motivation of this work has been to provide initial theoretical concepts to the experimentalists, some possible mechanisms have also been addressed to interpret the

experimental evidence, showing that LSSP may be nonthermal in nature and involve the laser radiation and the adspecies/surface in a synergistic selective process.

Before presenting the theoretical techniques concerned in this work, let us first pose some typical questions that essentially characterize the major features and dynamical nature of LSSP (see Fig.2):

1) How is the laser photon energy transferred to the pumped (active) mode(s) of the adspecies with subsequent relaxation to the bath (inactive) modes?

2) How are the excitation and relaxation dynamics of the adspecies/surface system characterized by the pumping rate, the damping (T_1 energy relaxation) kernel and the dephasing (T_2 phase relaxation) kernel?

3) How can a microscopic description of LSSP be semi-quantitatively reduced to a macroscopic description which in turn is tractable? What are the relevant ensemble-averaged quantities of the system?

4) How is the photon energy distributed in the pumped system, and is it thermally deposited in all the degrees of freedom of the system?

5) How does the intramolecular vibrational relaxation (IVR) rate play an essential role in the dynamical nature of LSSP (selective vs nonselective) via multiphonon processes? What are the requirements for a slow IVR rate which makes selective bond breaking possible?

Figure 2. Scheme showing the fundamental mechanism of LSSP.

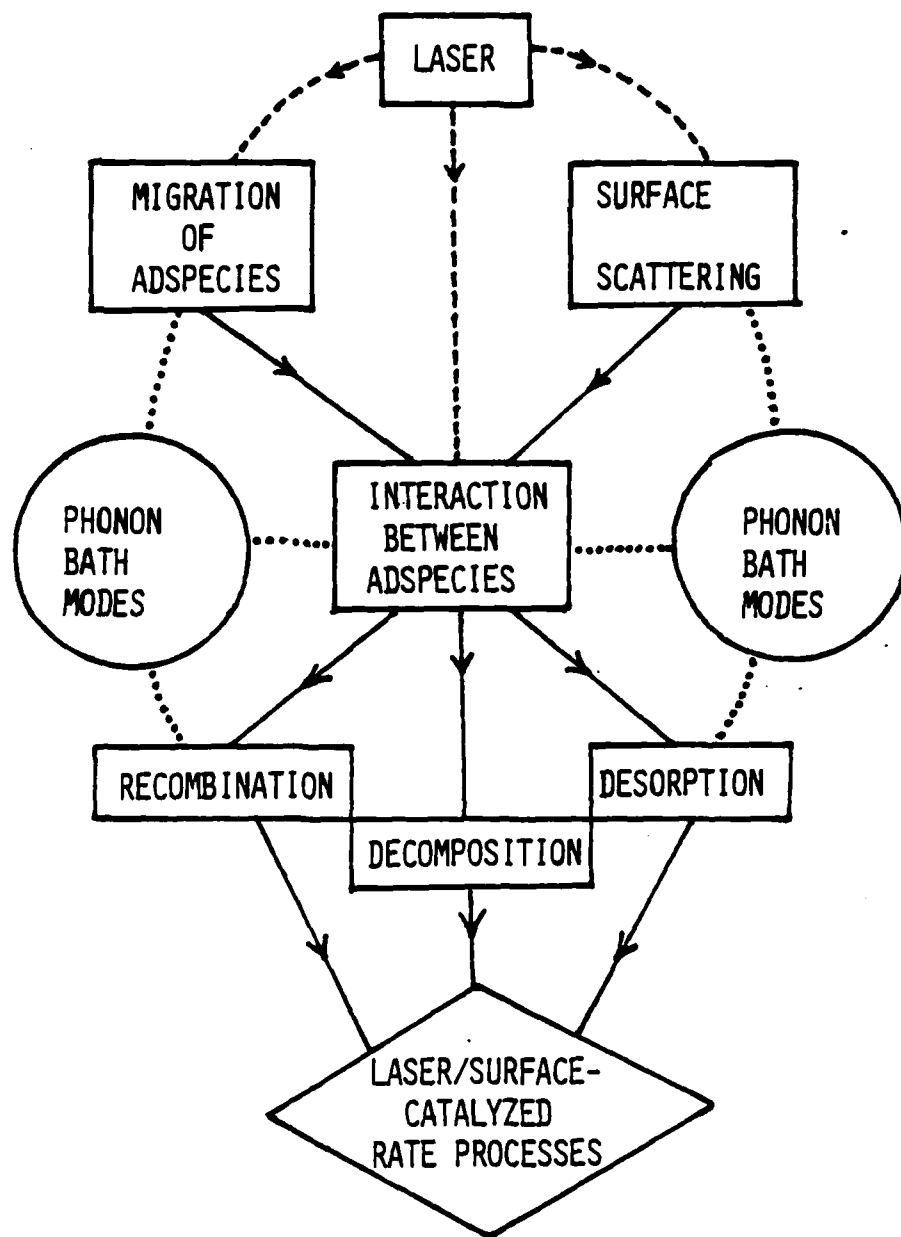


FIGURE 2

6) How might one control LSSP by means of selective excitations, and how can the substrate be effectively involved in a synergistic process for enhancing laser-assisted (or stimulated) heterogeneous catalysis?

While the last question has been only qualitatively studied due to its complexity in dynamics and the lack of complete surface information of an actual system, the remaining questions have been quantitatively or semiquantitatively attacked in this work. We note that questions (1) and (2) may be addressed by the absorption cross section (or the line shape) of the system, and questions (3) and (4) involve the many-body effects of the phonon modes and the related relative time scales of the radiative and relaxation processes. A flowchart of the methodology²⁴⁻³⁰ related to this work is shown in Fig.3, and the results of LSSP and heterogeneous catalysis based on these models (or approaches) are presented in Chapter III. We should point out that while the complicated models (e.g., the microscopic model Hamiltonian) provide a more rigorous quantitative description, the simple phenomenological models (e.g., the Langevin theory) give intuitive results of LSSP which are useful and attractive due to their simplicity.

Figure 3. Flowchart of methodology of LSSP.

FLOW CHART OF METHODOLOGY OF LSSP

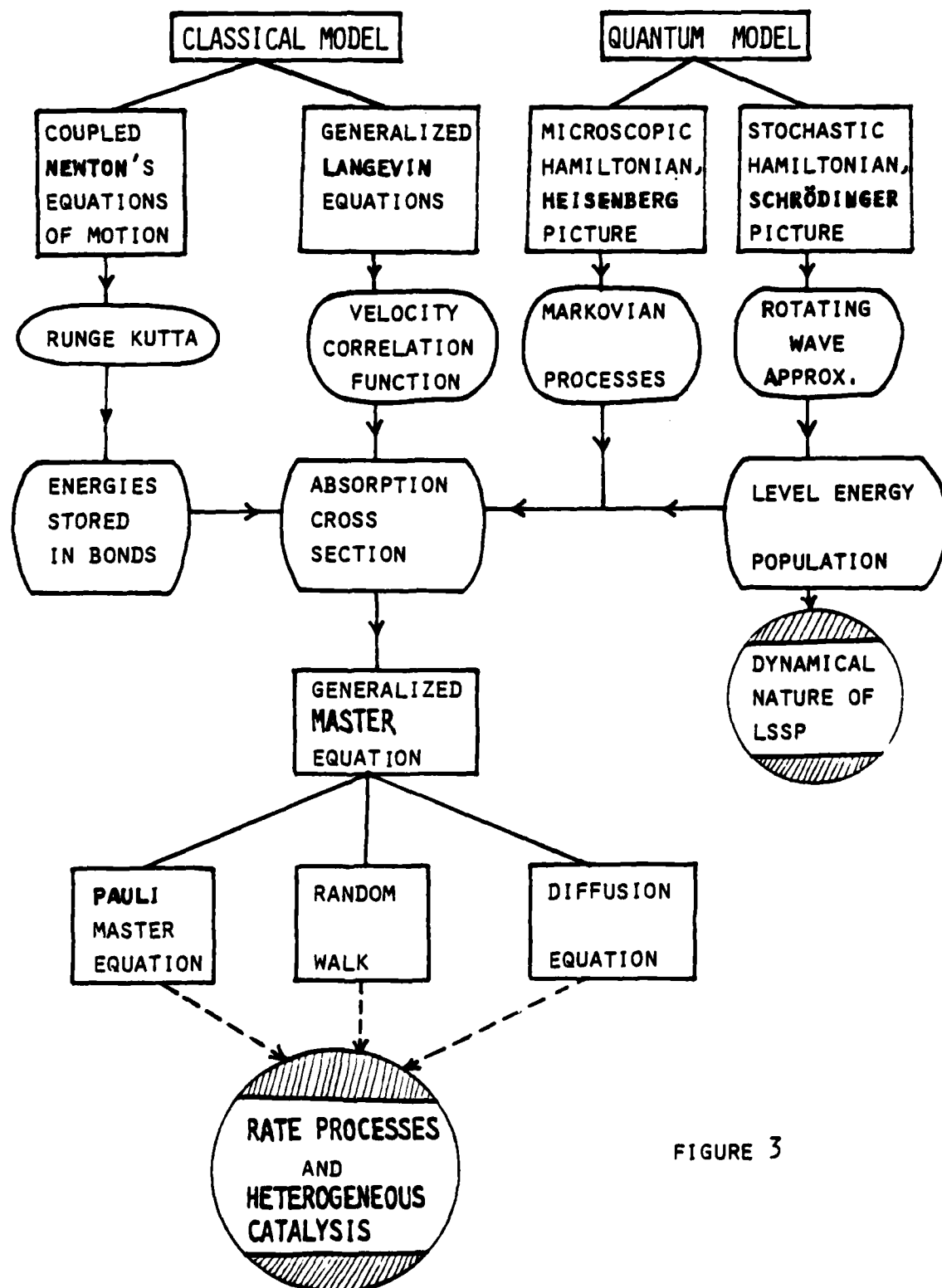


FIGURE 3

CHAPTER II

STOCHASTIC CLASSICAL MODELS OF MPA AND LASER-SELECTIVE EFFECTS

To study the nonlinear absorption cross section of MPA and its dynamical behavior, two phenomenological classical models are presented: (1) classical anharmonic model and (2) generalized Langevin dynamical model. Also, the laser-selective effects characterized by the multi-quantum exchange strength and the "internal resonant" condition are discussed. Only the "key" equations of the model systems and the major features of the results shall be shown in this chapter, since extensive details are available in the Appendices (in particular, Publications #1, 2 & 6 listed on page iv).

2.1 Classical Anharmonic Model^{1,6}

Here the IR-active mode of the polyatomic molecules is singled out and treated as an anharmonic oscillator governed by the classical equation of motion

$$\ddot{Q} + 2\Gamma\dot{Q} + \omega_0^2 Q + \alpha Q^2 + \beta Q^3 = f(t)/m, \quad (2.1)$$

where Q is the normal coordinate of the active mode (with reduced mass m), Γ is the damping factor (due to T_1 energy

relaxation), α and β are the small anharmonicities, and $f(t)$ is the driving force of the field.

Solving Eq.(2.1) via the harmonic balance method, we obtain the (time and ensemble) averaged power absorption, at near resonance, in a simple form:¹

$$\langle p \rangle = \left(\frac{qE}{4m} \right)^2 \left[\frac{\gamma + \Gamma}{(\Delta - K^* A^2)^2 + (\gamma + \Gamma)^2} \right], \quad (2.2)$$

where q is the classical charge, E is the electric field of the radiation, $\Delta = \omega_0 - \omega$ is the detuning, K^* is the anharmonicity and A is the steady-state amplitude of the oscillator, and γ and Γ are the damping factor and the dephasing-induced line broadening, respectively. We note that, in this simple model, the phase of the field is assumed to fluctuate while the relative phase of the oscillator remains fixed. However, the Lorentzian form in Eq.(2.2) will still be the same when a stochastically modulated frequency of the oscillator is introduced.^{2,7}

2.2 Generalized Langevin Theory^{2,25}

The dynamical behavior of MPA may be described by, instead of Eq.(2.1), the generalized Langevin equation (GLE) with memory effects:

$$\ddot{Q}(t) + \int_0^t \Lambda(t-t') \dot{Q}(t') dt' + \omega_{eff}^2 \int_0^t M(t-t') \dot{Q}(t') dt' = [f(t) + f_R(t)]/m. \quad (2.3)$$

$\Lambda(t)$ and $M(t)$ are the damping (T_1) kernel and the dephasing (T_2) kernel, respectively; ω_{eff} is the effective frequency of the active mode including anharmonicity and the bath-mode-induced frequency shift; $f(t)$ and $f_R(t)$ are the laser driving force and the bath-induced random force, respectively.

By solving for the Laplace-Fourier transform of the velocity autocorrelation function $F(t) \equiv \langle \dot{Q}(t) \dot{Q}(0) \rangle$, we are able to compute the temperature-dependent absorption cross section

$$\sigma(T, \omega) = \frac{4\pi^2 q^2}{c k \omega} (1 - e^{-\beta \hbar \omega}) (\text{Re } F[\omega]), \quad (2.4)$$

$$F[\omega] \equiv \int_0^\infty e^{-i\omega t} F(t) dt, \quad \beta = (kT)^{-1}, \quad (2.5)$$

which is characterized by the Laplace-Fourier transform of the autocorrelation function $F[\omega]$. For given forms of the memory functions $\Lambda(t)$ and $M(t)$, we may find the related Laplace-Fourier transforms and thus the function $F[\omega]$. In general, the cross section which reflects the general response of the system is rather complicated (see Publication #2 listed on page iv). For the simple limiting case of a Markovian process where the damping kernel contains no memory effects, the absorption cross section reduces to the fundamental Lorentzian form [Eq. (2.2)].

2.3 Laser-Selective Effects^{2,12}

The possibility of laser-selective chemistry was recently studied by Thiele, Goodman and Stone.¹⁶ Their restricted IVR model showed that selective bond breaking may be achieved by a line-broadening cutoff. In the present work, we propose a somewhat different and simpler model where the IVR rate is restricted by two factors: (i) a low-order multiquantum process and (ii) the near "internal resonant" condition. [For more details see Publications #2 & 12 listed on pages iv and v.] This implies that a rapid IVR rate (which decreases the absorption cross section) may be achieved only when both of the above requirements are fulfilled; otherwise, we expect a much slower IVR rate, which in turn cuts off the overall line broadening and makes selective bond breaking possible. A particular interesting example is the SF_6 system in which the rate of IVR for a three-quantum process (e.g., $\nu_3 \approx 2\nu_2 + \nu_6$, with ν_3 being the active mode) was found to be on the order of 10 picoseconds (or 3.3 cm^{-1}).³¹

CHAPTER III

CLASSICAL AND QUANTUM MODELS OF LSSP AND HETEROGENEOUS CATALYSIS

We shall consider a model system consisting of adspecies (atoms or molecules) initially chemisorbed on a solid surface and subject to low-power cw infrared radiation ($10\text{-}100\text{ W/cm}^2$). As mentioned in Chapter I, the interaction of the laser photons with a system depends not only upon the coherent nature of the field but also upon the heterogeneity of the substrate and the adspecies. We note that the complexity of LSSP, while being caused by the many-body effects of the surface phonons, is mainly due to the dynamical behavior of the excited adspecies - migration, desorption, recombination, surface scattering, etc. In an attempt to throw some light on LSSP, whose complexity rules out any "first-principles" treatment, we examine some phenomenological and semiquantitative models (see the methodology shown in Fig.3 on page 11) which allow us to compute physically significant quantities, such as the average power absorption and desorption probabilities. In addition, the dynamical behavior and the nature of LSSP are investigated via the microscopic model Hamiltonian and quantum kinetic approaches.

There are seven more sections in this chapter: microscopic model Hamiltonians #1 and #2, selective vs nonselective nature of LSSP, energy populations and desorption dynamics, classical models #1 and #2, and the possibility of controlling

surface processes by laser radiation. Most of the above subjects are shown, with more extensive details, in the Appendices. We shall show in this chapter just the key equations characterized the primary results of LSSP, except in Sections 3.2, 3.6 and 3.7, where some results are presented which do not appear in the Appendices.

3.1 Microscopic Model Hamiltonian #1: Multiphoton-Multiphonon Processes^{7,10}

The microscopic Hamiltonian describing a group of ad-species chemisorbed on a solid surface and driven by infrared radiation may be expressed as

$$H^I(t) = H_A + H_B + H_{AA} + H_{AB} + H_{ABA} + H_{AF} . \quad (3.1)$$

H_A and H_B are the unperturbed Hamiltonian of the active (A) mode and the bath (B) modes, respectively; H_{AA} and H_{AB} represent the direct mode-mode interactions of the active-active and the active-bath, respectively; H_{ABA} denotes the indirect interaction among the active modes mediated by the bath (phonon) modes; and H_{AF} is the coupling of the laser field with the active dipoles of the adspecies.

To study the energy-transfer processes governed by Eq. (3.1), we shall first set up the equations of motion of the relevant operators of the active and bath modes in the Heisenberg

picture, where the microscopic Hamiltonian is expressed in a second-quantization form. By employing the Markovian approximation and Kubo's cumulant expansion technique, we are able to solve a set of coupled equations of motion, where the many-body effects of the bath phonon modes are effectively replaced by a damping factor in the Heisenberg-Markovian picture (HMP), including no memory effects. This is the physical situation where the correlation time of the bath modes is much faster than any other time scales of the radiative processes, with no significant energy feedback from the bath modes to the pumped mode. We are then interested in the ensemble-averaged energy absorption of the pumped modes instead of the detailed individual absorptions of the adspecies.

The primary features of the multiphoton-multiphonon processes are characterized by the nonlinear equation for the averaged excitation $\langle n \rangle$, in the adiabatic approximation,^{6,10}

$$\frac{d\langle n \rangle}{dt} = \frac{A I (\gamma_1 + \gamma_2)}{(\Delta - 2\varepsilon^* \langle n \rangle)^2 + (\gamma_1 + \gamma_2)^2/4} - \gamma_1 (\langle n \rangle - \bar{n}), \quad (3.2)$$

where $\langle n \rangle$ and \bar{n} are the averaged excitation of the pumped mode and the bath modes, respectively, γ_1 and γ_2 are the T_1 (energy) and T_2 (phase) relaxation rate, respectively, and I is the laser intensity. We note that the input power of the total system [given by the first term of Eq.(3.2)] is essentially characterized by an asymmetric Lorentzian and is proportional

to the laser intensity. Thus, for a field-free system, the steady-state average excitation $\langle n \rangle$ is \bar{n} , which is simply the Bose-Einstein distribution. One of the important features indicated by Eq.(3.2) is that the bath-induced damping factor γ_1 , characterized by the multiphonon coupling strength and the associated density of states of the bath modes, enables us to investigate the selective nature of LSSP quantitatively. For a process with high selectivity, we expect a small damping factor, which may be achieved by a high-order multiphonon coupling or a far off "internal resonant" process.¹² Such selective effects and the results of Section 2.3 are consistent with the concept of the "energy-gap law" given by Nitzan et al.³

3.2 Microscopic Model Hamiltonian #2: Laser-Stimulated Migration

The model Hamiltonian #1 [given by Eq.(3.1)], containing most of the interactions of LSSP (both direct and surface-mediated indirect interactions of the adspecies), can be used to describe the ensemble-averaged behavior of the adspecies, but not (explicitly) their individual behavior, e.g., intersite transitions (migration). This is the situation of a strongly trapped case with high adspecies coverage, such that energy transfer with laser photons is not significantly affected by surface migration of the individual adspecies. However, for

a low-coverage system, the mobility of the adspecies (and hence LSSP dynamics) may be greatly enhanced by the laser.

To study the dynamical behavior of LSSP including laser-stimulated migration, we present the model Hamiltonian #2. We begin with the dynamical Hamiltonian

$$H^D(t) = H_0(Q_1, Q_2, \dots, Q_j) + \sum_{k, k'} V_{kk'}(Q_1, Q_2, \dots, Q_j) C_k^\dagger C_{k'} + H_{AF} \quad (3.3)$$

where H_0 is the unperturbed Hamiltonian of the system (with the normal coordinate Q_j), $V_{kk'}(Q_j)$ is the (lattice-site-dependent) interaction potential of the system, and C_k^\dagger and C_k are the site-operators of the Bloch states $|\vec{k}\rangle$ and $\langle \vec{k}'|$, respectively, which can be expressed in terms of the Wannier function (or site-representation) by³²

$$C_k^\dagger \equiv |\vec{k}\rangle = \frac{1}{\sqrt{N}} \sum_m e^{i\vec{k} \cdot \vec{R}_m} |n\rangle, \quad (3.4)$$

$$C_k \equiv \langle \vec{k}'| = \frac{1}{\sqrt{N}} \sum_m e^{-i\vec{k}' \cdot \vec{R}_m} \langle m|. \quad (3.5)$$

The Taylor expansion of the interaction potential

$$V_{kk'}(Q_1, Q_2, \dots, Q_j) = V_0 + \sum_{j=1}^{\infty} \left(\frac{\partial V}{\partial Q_j} \right)_0 Q_j + \dots + \sum_{\substack{p \\ \sum_j p_j = p}} \frac{1}{p!} \left(\frac{\partial^p V}{\partial Q_1 \partial Q_2 \dots \partial Q_j} \right)_0 Q_1^{p_1} Q_2^{p_2} \dots Q_j^{p_j} + \dots \quad (3.6)$$

gives us the general forms for the intramolecular couplings with the order p of the multiphonon processes. Using the second-quantization expression of Eq.(3.6) and the Wannier

site-representation in Eqs. (3.4) and (3.5), we obtain, from Eq. (3.3), the microscopic model Hamiltonian #2 as follows:

$$H^{II}(t) = H_A^0 + H_B^0 + H_C^0 + H_C' + H_1 + H_2 + H_3 + H_4 + H_{AF}, \quad (3.7)$$

$$H_A^0 = \hbar\omega_A a^\dagger a, \quad H_B^0 = \sum_j \hbar\omega_j b_j^\dagger b_j, \quad H_C^0 = \sum_n \hbar\omega_n c_n^\dagger c_n, \quad (3.8)$$

$$H_C' = \sum_{j,j'} X_{nj} c_n^\dagger c_n (b_j^\dagger + b_j) + \sum_n Y_n c_n^\dagger c_n (a^\dagger + a) + \sum_{nj} Z_{nj} c_n^\dagger c_n (a^\dagger + a)(b_j^\dagger + b_j), \quad (3.9)$$

$$H_1 = \sum_{n \neq m} J_{nm} c_n^\dagger c_m, \quad (3.10)$$

$$H_2 = \sum_{n \neq m} K_{nm} c_n^\dagger c_m (a^\dagger + a), \quad (3.11)$$

$$H_3 = \sum_j \sum_{n \neq m} G_{nm}^j c_n^\dagger c_m (b_j^\dagger + b_j), \quad (3.12)$$

$$H_4 = \sum_j \sum_{n \neq m} W_{nm}^j c_n^\dagger c_m (a^\dagger + a)(b_j^\dagger + b_j) + [\text{higher-order terms}], \quad (3.13)$$

$$H_{AF}(t) = f_i(t) (a^\dagger + a) + \sum_j f_j(t) (b_j^\dagger + b_j) + \dots \quad (3.14)$$

The coupling parameters X_{nj} , Y_n , Z_{nj} , J_{nm} , K_{nm} , G_{nm}^j and W_{nm}^j are related to the derivatives of the interaction potential $V(Q_j)$ by

$$G_{nm}^j = F_{nm} X_{nj} = F_{nm} \left(\frac{\partial V}{\partial Q_j} \right)_0 \alpha_j, \quad (3.15)$$

$$K_{nm} = F_{nm} Y_n = F_{nm} \left(\frac{\partial V}{\partial Q_A} \right)_0 \alpha_A, \quad (3.16)$$

$$W_{nm}^j = F_{nm} Z_{nj} = F_{nm} \left(\frac{\partial^2 V}{\partial Q_A \partial Q_j} \right)_0 \alpha_A \alpha_j, \quad (3.17)$$

$$J_{nm} = F_{nm} V_0, \quad F_{nm} = \frac{1}{N} e^{i \vec{k} \cdot (\vec{R}_n - \vec{R}_m)}, \quad (3.18)$$

$$\alpha_A = [\hbar/(2m_A \omega_A)]^{1/2}, \quad \alpha_j = [\hbar/(2m_j \omega_j)]^{1/2}. \quad (3.19)$$

The above microscopic Hamiltonian, while complicated, is a general form describing not only the intramolecular anharmonic couplings but also the dynamical interactions of LSSP. We shall not here attempt to solve the coupled equations of motion of the operators a^\dagger , b^\dagger and $c^\dagger c$, etc., but rather concentrate on a phenomenological approach to account for the effects of the excitation-induced migration. It has been shown that the effects of the surface migration for Markovian processes may be characterized by another damping factor γ_{η} , distinguished from the γ_1 damping factor induced by the intramolecular coupling.^{7,13} Therefore, the overall line broadening of the dynamical system [governed by Eq.(3.7)] may be achieved not only by the usual T_1 and T_2 relaxation but also by the migration-induced broadening γ_{η} . Furthermore, using Eq.(3.7), one can describe rigorously the laser-enhanced surface migration by employing the generalized master equation (GME) and the continuous time random-walk (CTRM) techniques.^{9,27,28}

3.3 Selective vs Nonselective LSSP^{8,9}

We now consider a multilevel system consisting of the active (A) mode (with highest frequency ω_A), the B modes (with intermediate mean frequency ω_B), and the bath (C) modes (with lowest frequencies and condensed states) as shown in Figs.4 and 5. The active mode is pumped by the laser field (with the pumping rate V) and relaxes its energy to the B modes via

Figure 4. Schematic representation of energy transfer processes for LSSP of a model system consisting of the active (A) mode, B modes and the condensed bath (C) modes.

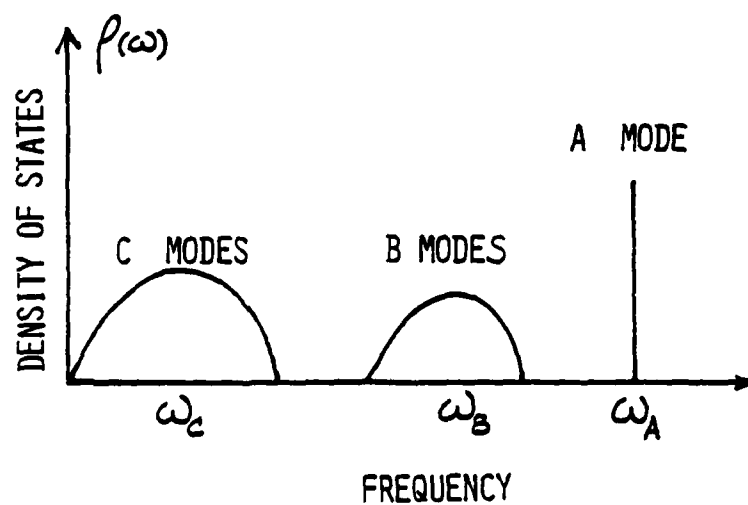
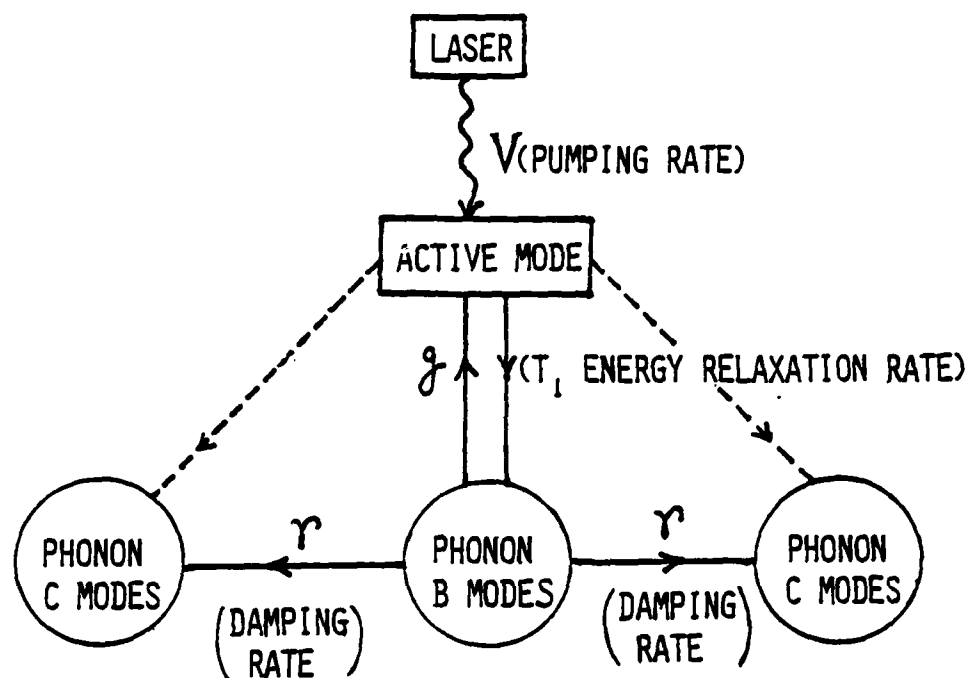


FIGURE 4

Figure 5. Schematic energy level diagrams of a model system.

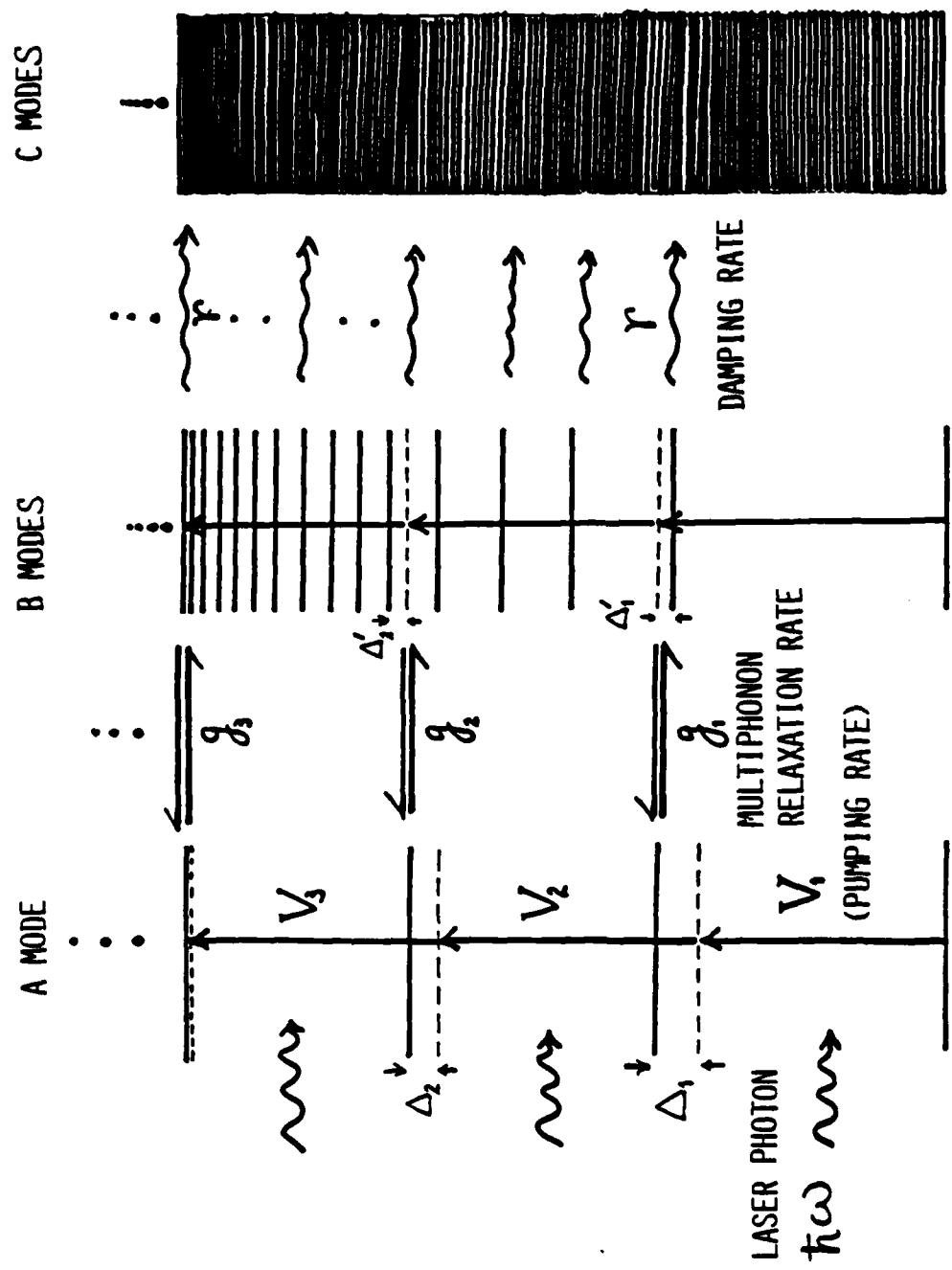


FIGURE 5

a multiphonon coupling factor g . The photon energy stored in the B modes gradually leaks to the condensed C modes with a damping rate γ . The dynamical nature of LSSP, characterized by the level populations P_A (for the active mode), P_B (for the B modes) and P_C (for the C modes) is seen in Fig.6 for different sets of the pumping rate (V), the coupling factor (g) and the damping rate (γ). Selective excitation of the active mode [with $(V, |g|, \gamma) = (4, 0.1, 0.4)$] and nonselective thermal heating of the C modes [with $(V, |g|, \gamma) = (4, 1, 1)$] are shown in Fig. 6 (A) and (B), respectively.

We note that the lifetimes of the level populations are in the range of microseonds (with corresponding pumping rate $V = 10^8 - 10^9 \text{ sec}^{-1}$ or laser intensity $I = 10 - 100 \text{ W/cm}^2$), which are much longer than those of gas-phase picosecond phenomena (with high-power pumping rate $V = 10^{11} - 10^{12} \text{ sec}^{-1}$). This is one of the important features of LSSP, where a low-power cw laser can be used to induce interesting chemical dynamics.

3.4 Energy Populations and Desorption Dynamics^{6,7}

Within the context of laser-stimulated desorption, there are two relevant variables: (i) the energy stored in the active mode(s) and (ii) the total energy content of the whole adspecies. Thus, in the master (rate) equation approach, the energy population function may be defined in the energy space of either the pumped mode or the whole adspecies, depending on the parameters chosen to describe the processes. For

Figure 6. Level populations of the A, B and C modes of two-photon multiphonon processes for $(V, |g|, \gamma) = (A) (4, 0.1, 0.4)$ and $(B) (4, 1, 1)$.

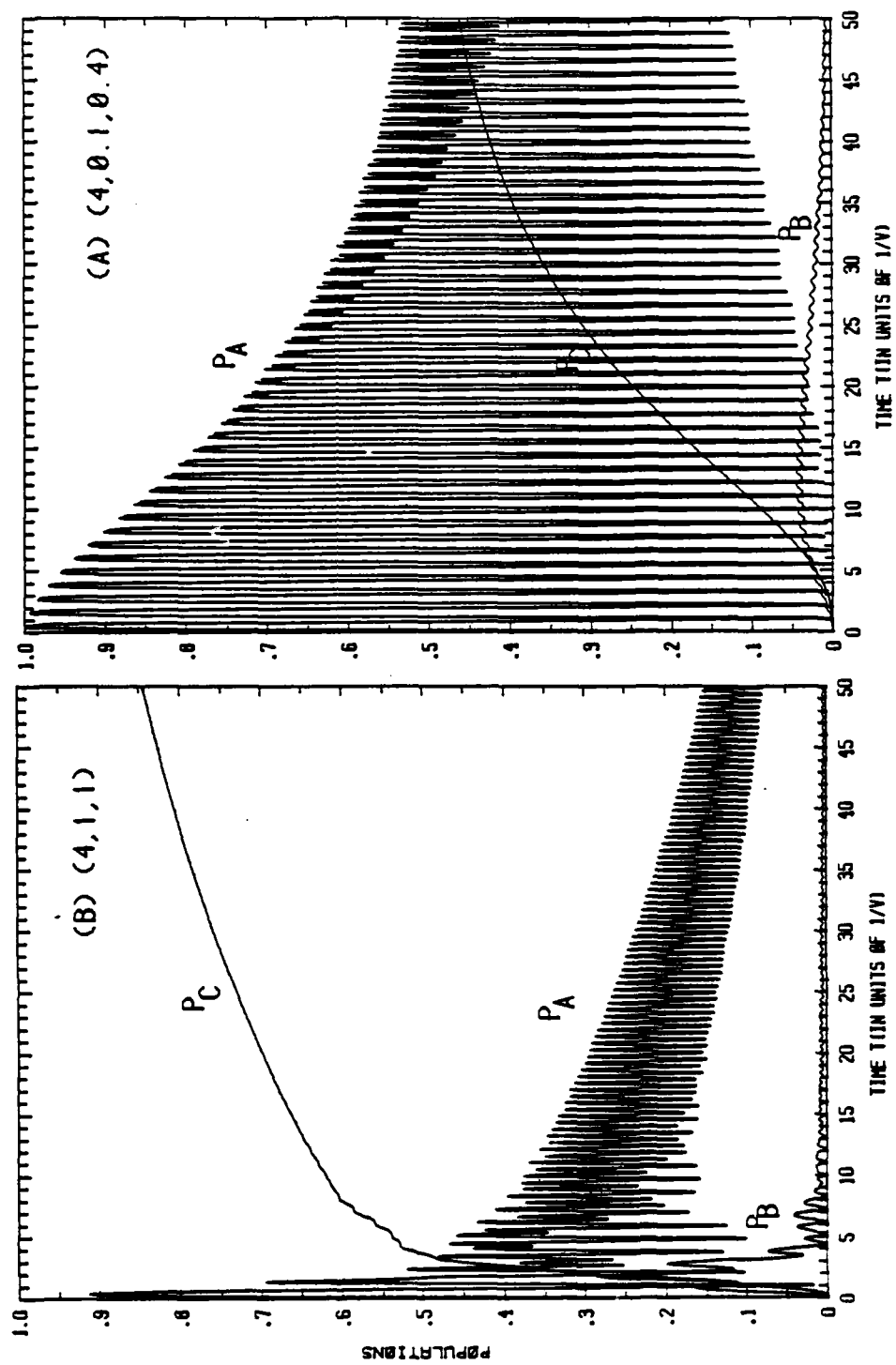


FIGURE 6

a system with a fast IVR rate, the relevant parameter would be the number of photon absorbed by the whole adspecies, while for a slow IVR rate, the number of photons deposited in the pumped mode may be the relevant parameter. In general, knowing this parameter (i.e., the energy population, which is characterized by the absorption cross section embodied in the rate equation), we can evaluate the desorption probability P_d as given by

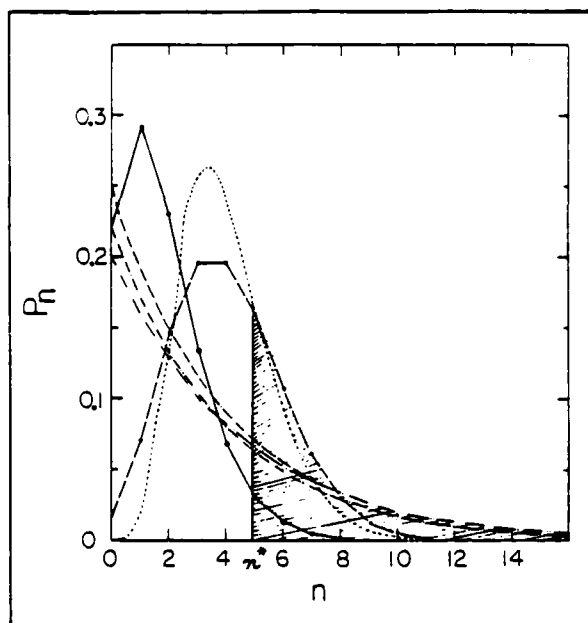
$$P_d = 1 - \sum_{n=0}^{n^*-1} P_n = 1 - \int_0^{n^*} P_n dn . \quad (3.20)$$

P_n is the population of the system in the n (energy) space, and n^* is the desorption threshold, i.e., the adspecies will be desorbed from the solid surface by absorbing n^* laser photons. Several population functions and the associated desorption probabilities are shown in Fig. 7.[For the derivation of the populations from the rate equation and detailed discussion, see Publications #6 & 7 listed on page iv.]

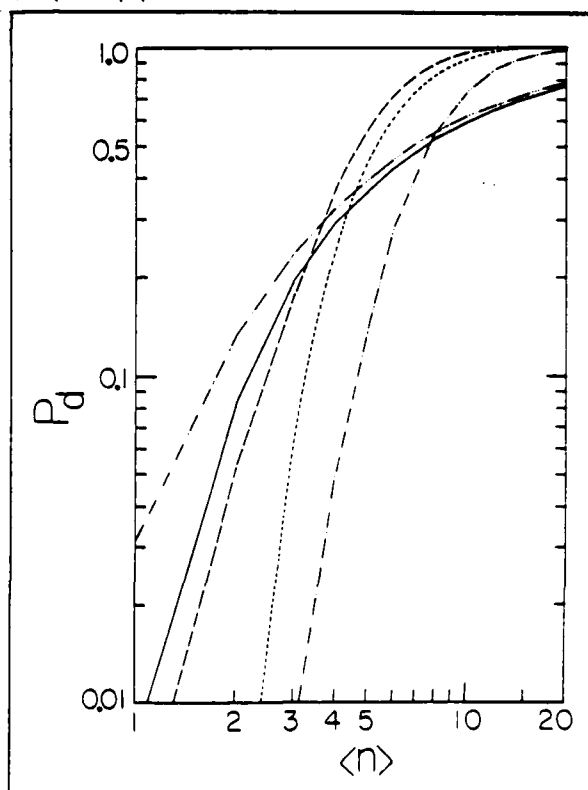
3.5 Classical Model #1: Generalized Langevin Theory¹²

As previously mentioned, one of the major concerns of LSSP is how the absorption cross section, which reflects the level structure and the IVR rate of the system, is affected by the excitation and relaxation dynamics. To study the dynamical cross section (which governs the IR line shape), we

Figure 7. Energy distribution functions and the corresponding desorption probabilities obtained from the rate equation in energy space.



The distribution functions of four-photon excitations ($\langle n \rangle = 4$), for Poisson population (—), diffusion model population with $S=1$ (---) and $S=6$ (---), Boltzmann population with $S=1$ (-·-·-) and $S=6$ (---), and quantal population with $S = \alpha = 1$ (-·-·-).



The desorption probabilities of $n^*=5$ for Poisson distribution (—), diffusion model with $\beta=1$, $S=6$ (---), Boltzmann distributions with $S=6$ (-·-·-) and $S=1$ (---), and quantal model with $\alpha = S = 1$ (-·-·-).

FIGURE 7

present the generalized Langevin equation (GLE) for a model system consisting of a group of interacting active modes coupled to the condensed bath modes:

$$\begin{aligned} \ddot{f}_j(t) + \ddot{f}_j^R(t) = m_j \ddot{Q}(t) + m_j \int_0^t \beta(t-t') \dot{Q}_j(t') dt' \\ + m_j \bar{\Omega}_j^2 \int_0^t M_j(t-t') \dot{Q}_j(t') dt' - \sum_{i \neq j} \int_0^t N_{ij}(t-t') \dot{Q}_i(t') dt'. \end{aligned} \quad (3.21)$$

Q_j is the normal coordinate of the subsystem (total system excluding the bath modes); $\bar{\Omega}_j$ is the effective frequency including the anharmonicity and the bath-induced frequency-shift; $\beta_j(t)$ and $M_j(t)$ are, respectively, the damping kernel and dephasing kernel describing the interaction dynamics between the subsystem and the bath modes; $N_{ij}(t)$ represents the interaction function between the i -th and j -th modes of the subsystem; $f_j(t)$ and $f_j^R(t)$ are, respectively, the laser driving force and the bath-induced random force acting on the j -th mode.

By linear response theory, we find the temperature-dependent cross section to be¹²

$$\sigma(T_0, \omega) = \sigma(T_0) \sum_{i,j} (q_i q_j E_i E_j) (\text{Re } F_{ij}(\omega)), \quad (3.22)$$

which is characterized by the classical charge (q_k), the effective electric field (E_k) acting on the k -th active mode, and the real part of the Laplace-Fourier transform of the

velocity correlation function $F_{ij}[\omega]$ defined by

$$F_{ij}[\omega] \equiv \int_0^t e^{-i\omega t} F_{ij}(t) dt, \quad (3.23.a)$$

$$F_{ij}(t) = \langle \dot{Q}_i(t) \dot{Q}_j(t) \rangle. \quad (3.23.b)$$

For given forms of the memory functions $\beta_j(t)$, $M_j(t)$ and $N_{ij}(t)$, we can find the corresponding Laplace-Fourier transforms, yielding the function $F[\omega]$ and thus the cross section. A detailed examination of the cross section for non-Markovian (with memory effects) and Markovian [without memory effects, or $\beta_j = \beta_0 \delta(t)$] processes is given in Publication #12 listed on page v. We here point out one of the important features of LSSP governed by GLE as follows: the dynamical transition of LSSP (from coherent to incoherent) may be described by the relaxation parameters contained in the cross section, which reflects not only the internal level structure of the excited mode (i.e., the heterogeneity of the adspecies/surface system) but also the surface dynamics of the excited adspecies, e.g., migration, diffusion, desorption and rate processes.

3.6 Classical Model #2: Numerical Simulation of CO/Ni

We now consider a model system of CO chemisorbed on a nickel surface and subject to IR laser radiation (with field frequency near resonant to the stretching frequency of CO), restricting ourselves to a truncated five-atom chain O-C-Ni-

Ni-Ni assigned as atom-1, -2, etc. The coupled Newton's equations of motion describing this system are

$$m_1 \ddot{x}_1 = -k_{12}(x_1 - x_2) - \gamma \dot{x}_1 - f(t), \quad (3.24)$$

$$m_2 \ddot{x}_2 = -k_{12}(x_2 - x_1) - k_{23}(x_2 - x_3) - \gamma \dot{x}_2 + f(t), \quad (3.25)$$

$$m_3 \ddot{x}_3 = -k_{23}(x_3 - x_2) - k_5(x_3 - x_4) - \gamma \dot{x}_3, \quad (3.26)$$

$$m_4 \ddot{x}_4 = -k_5(x_4 - x_3) - k_5(x_4 - x_5) - \gamma \dot{x}_4, \quad (3.27)$$

$$m_5 \ddot{x}_5 = -k_5(x_5 - x_4) - \gamma \dot{x}_5, \quad (3.28)$$

where k and γ are the force constant and the damping factor (due to surface and bulk atoms of the system), respectively, and $f(t) = qE \sin(\omega t)$ is the laser driving force. The force constants used here are: $k_{12} = 16.8$, $k_{23} = 2.6$ and $k_5 = 0.24$ (in units of mdyne/Å), and the atom masses are $m_1=16$, $m_2=12$, and $m_3=58.71$ (amu), where $k_s = k_{34} = k_{45}$, and $m_s = m_3 = m_4 = m_5$.

These five coupled second-order differential equations are equivalent to a set of ten coupled first-order differential equations, which have been numerically solved by the Runge-Kutta method. In addition to the amplitudes of the chain atoms, we can simulate the bond energies stored in the system by

$$E_A = \sum_{i=1}^2 \left[\frac{1}{2} m_i \dot{x}_i^2 + \frac{1}{2} k_{12} (x_1 - x_2)^2 \right], \quad (3.29)$$

$$E_B = \frac{1}{2} m_3 \dot{x}_3^2 + \frac{1}{2} k_{23} (x_2 - x_3)^2, \quad (3.30)$$

$$E_C = \sum_{i=4}^5 \left[\frac{1}{2} m_i \dot{x}_i^2 + \frac{1}{2} k_5 [(x_3 - x_4)^2 + (x_4 - x_5)^2] \right]. \quad (3.31)$$

The numerically simulated results for the amplitudes of the atoms and the energy profiles of different bonds are plotted in Fig. 8 (A)-(D) for different sets of values of the damping factor γ and the detuning $\Delta = \omega_0 - \omega$. Fig. 8(A) shows the exact-resonant case ($\Delta = 0$) with $\gamma = 100 \text{ cm}^{-1}$. The near-resonant cases are shown in Fig. 8(B) with $\gamma = 100 \text{ cm}^{-1}$ and $\Delta = 20 \text{ cm}^{-1}$, Fig. 8(C) with $\gamma = \Delta = 10 \text{ cm}^{-1}$, and Fig. 8(D) with $\gamma = \Delta = 0$. It is seen that the decaying and oscillating features of the energy profiles are characterized by the damping factor and the detuning, respectively. We note that the amplitudes of the excited CO molecule are much higher than those of the Ni atoms due to the mass differences [atom-2 has the highest amplitude]. The energy profiles shown in Fig. 8 are generated for a high-power laser with intensity $I = 10^{12} \text{ W/cm}^2$ (hence short computation times, in contrast to the situation of a low-power laser). Due to the high frequency of the field $\omega = 10^{14} \text{ sec}^{-1}$, we require time steps on the order of 10^{-15} sec in using the Runge Kutta method. For an actual system of low-power excitation LSSP (with laser intensity $I = 10\text{-}100 \text{ W/cm}^2$), we expect similar energy profiles as shown in the high-power cases by realizing the fact that the energy profiles shown in Fig. 8 are "universal" for any ranges of laser power, provided the proper time scales (in units of the reciprocal of the pumping rates) are chosen.¹¹

Figure 8. Amplitudes of atoms and energy profiles for different bonds of the CO/Ni system, subject to a high-power laser with intensity $I = 10^{12}$ W/cm², for different sets of the damping factor (γ) and the detuning (Δ): (A) $\gamma = 100\text{cm}^{-1}$ for exact resonance $\Delta = 0$, (B) $\gamma = 100\text{cm}^{-1}$, $\Delta = 20\text{cm}^{-1}$, (C) $\gamma = \Delta = 10\text{cm}^{-1}$, (D) $\gamma = \Delta \approx 0$.

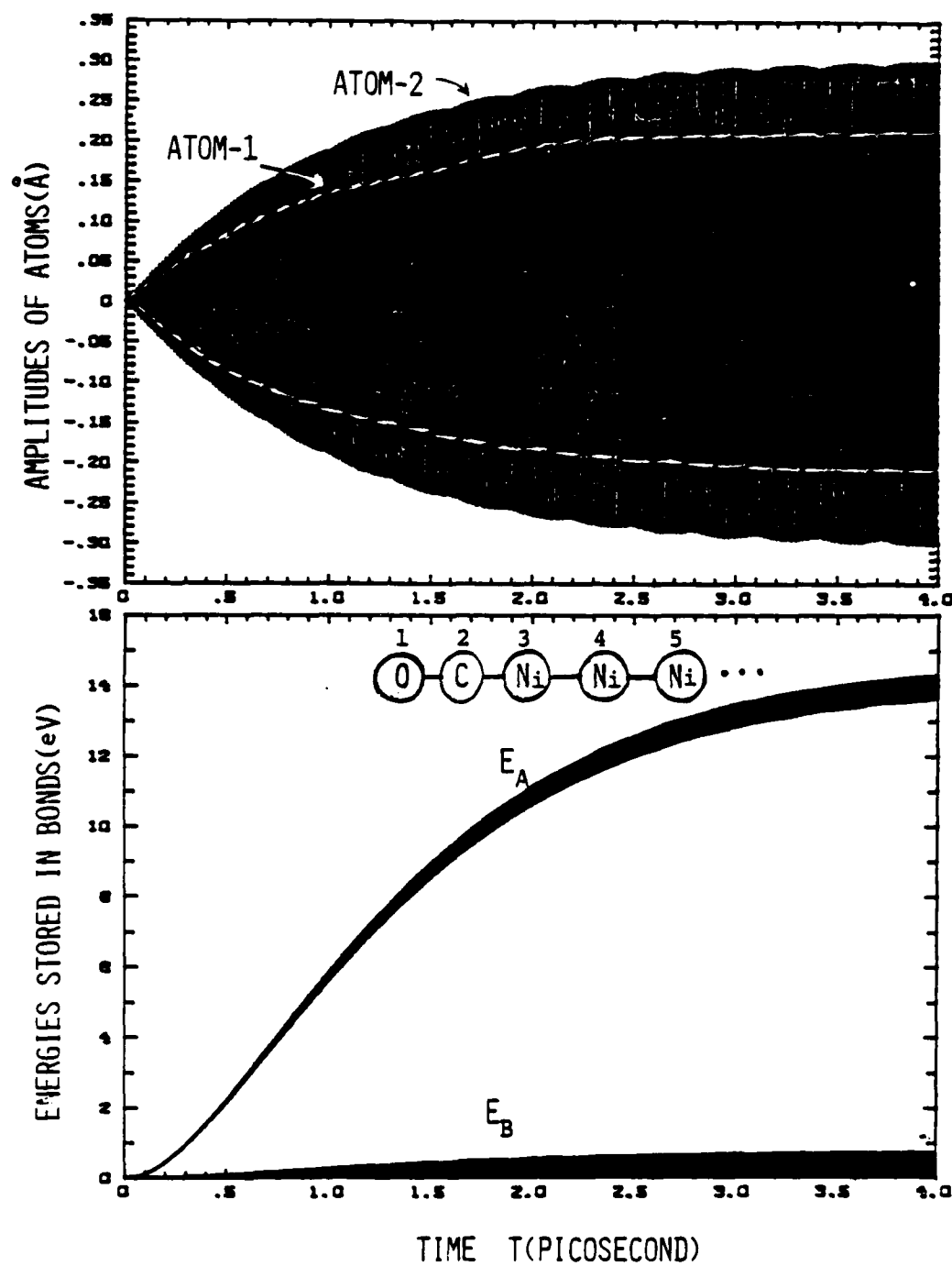


FIG. 8(A)

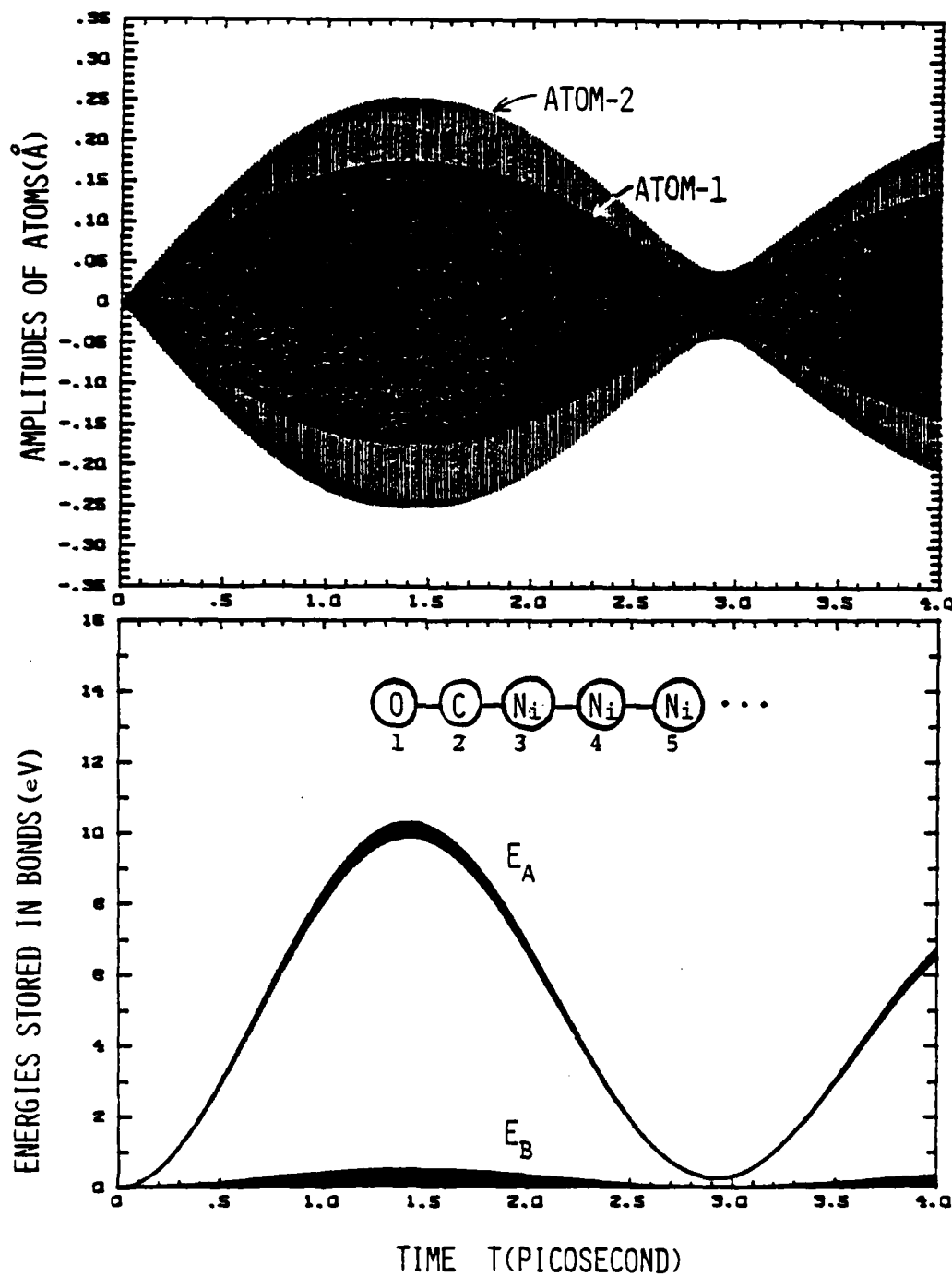


Fig. 8(B)

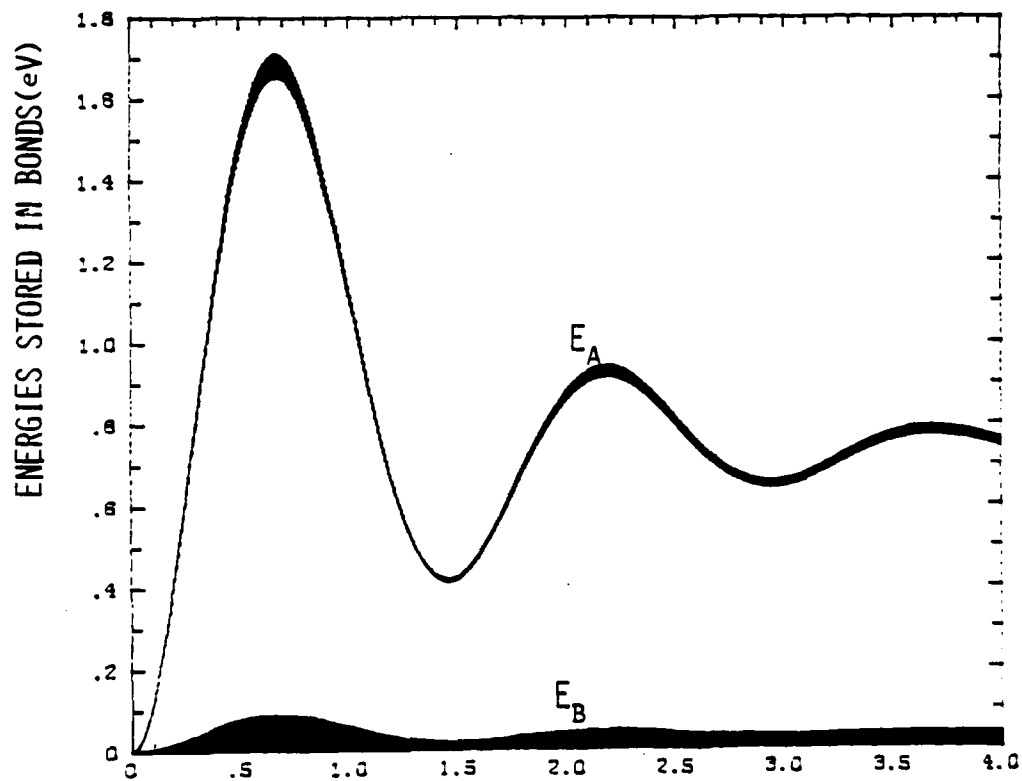
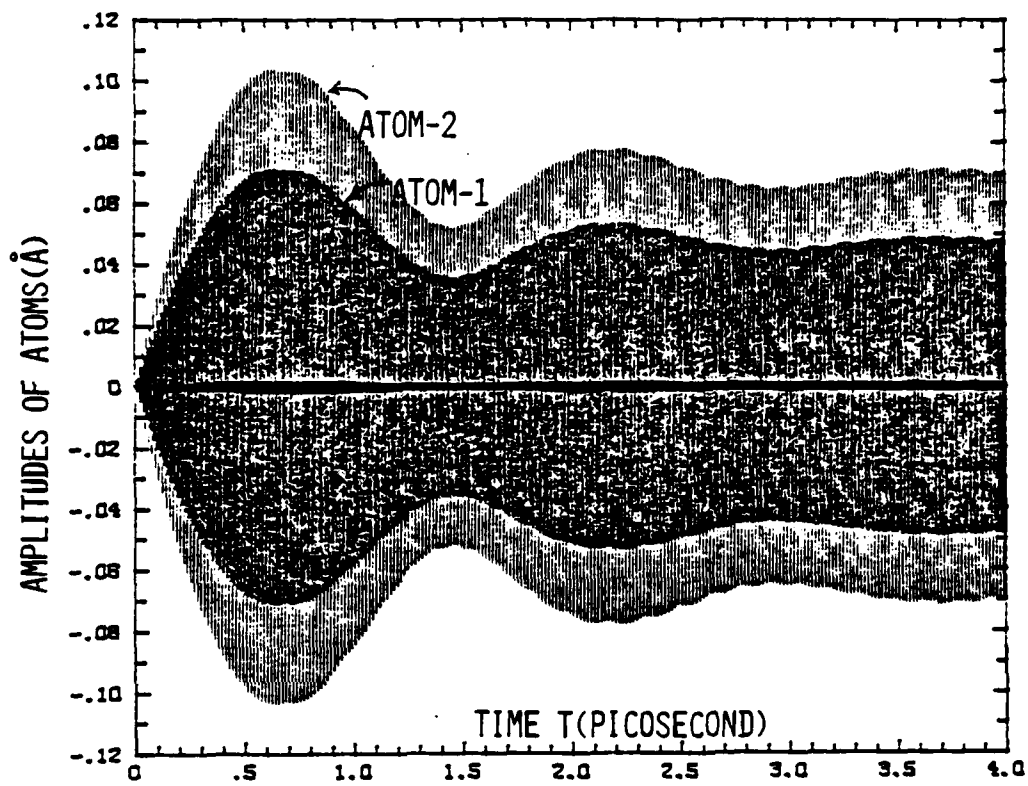


FIG. 8(C)

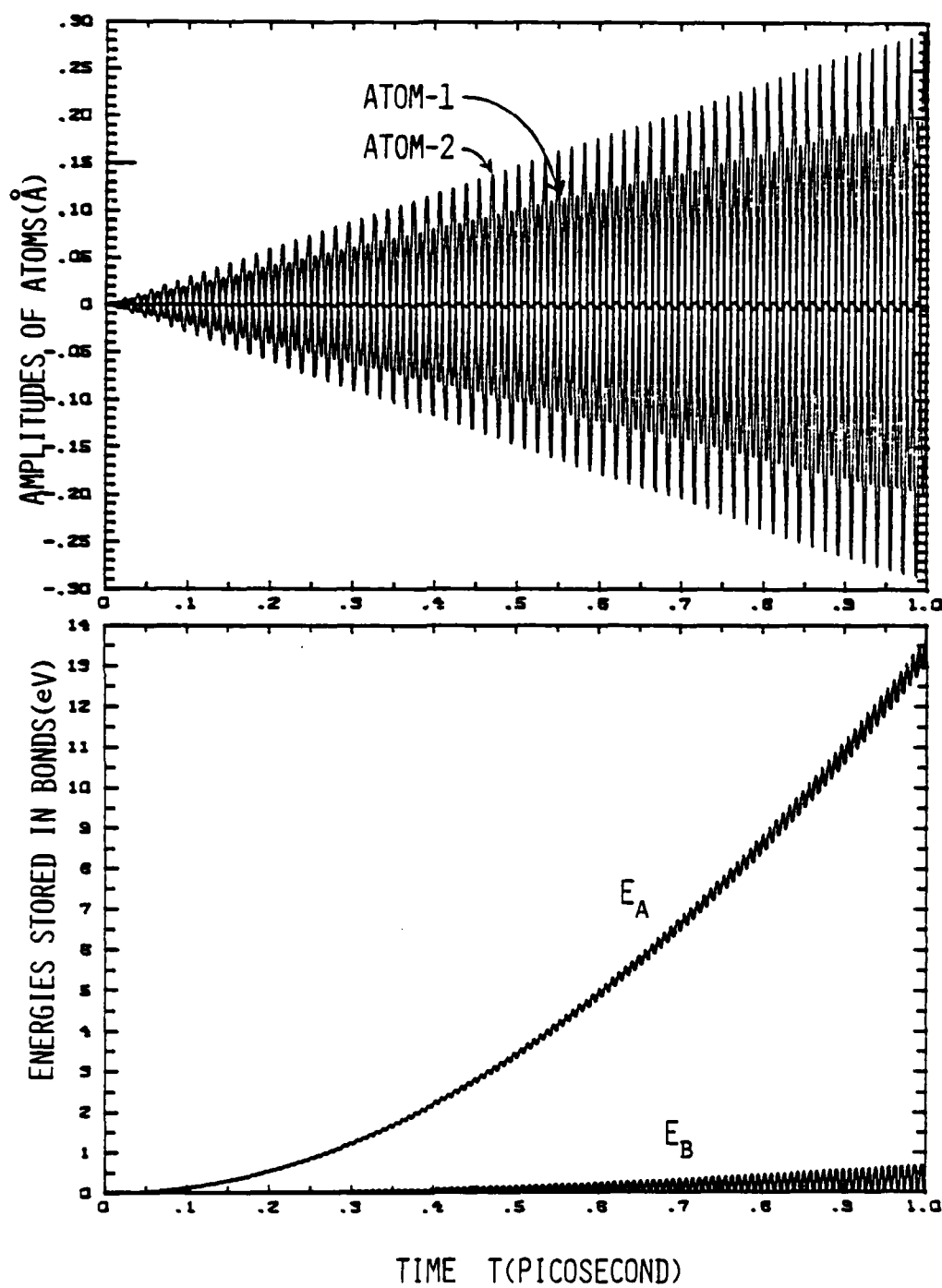


FIG. 8(D)

3.7 On the Possibility of Controlling Surface Processes by Laser Radiation

Based on the theoretical framework presented in the previous sections, we can study the possibility of laser-controlled surface processes (migration, desorption and heterogeneous catalysis).

A. Laser-Controlled Surface Concentration of a Multicomponent System³

By employing the laser-stimulated generalized Langmuir kinetic equation (LSGLE), we obtain the steady-state partial pressure of the i -th component of a heterogeneous system with multicomponent species chemisorbed on a surface as:

$$p_i = K z^{1-y} \theta^x / (1-\theta)^y, \quad (3.32)$$

where K is the laser-stimulated desorption rate constant, θ is the fractional coverage of the selectively-excited i -th component of the adspecies, x and y are the kinetic order and the occupancy order, respectively, and z denotes the number of nearest-neighbors for each unoccupied lattice site.

An important feature of Eq.(3.32) is: for low surface temperature, we may avoid spontaneous nonselective thermal desorption and control the surface concentration of the desired adspecies, and hence study the heterogeneity of the surface such as the composition and location of the active center of the catalytic substrate.

B. Laser-Stimulated Heterogeneous Catalysis

As addressed in Section 1.2, the mechanism of heterogeneous catalysis involves these surface steps: adsorption, migration, and recombination and rate processes in either dissociative or associative states. The adsorption states of the adspecies can be further divided into the chemisorbed and physisorbed (precursor) state. Each step of a catalytic process has an activation energy associated with it. Fig.9 illustrates the schematic potential energy of a diatomic molecule AB adsorbed on a metal surface, where the combination of the potential energy curve of "AB + metal" and that of "A + B + metal" gives rise to an energy barrier between a shallow physisorbed state for AB and a deeper chemisorbed state for A + B. The laser can enhance a rate process by either decreasing its activation energy or increasing the preexponential factor from the point view of transition state theory.²³ We shall discuss some prototypes of the laser-stimulated surface processes below.

(1) Laser/Surface-Catalyzed Recombination and Rate Processes

Consider the mechanism of incident atom A acting on an adsorbed atom B on the catalyst surface (K):

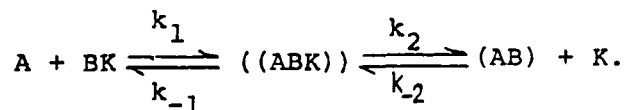


Figure 9. Schematic diagram of the potential energy $E(R)$ showing the adsorption states of the adspecies.

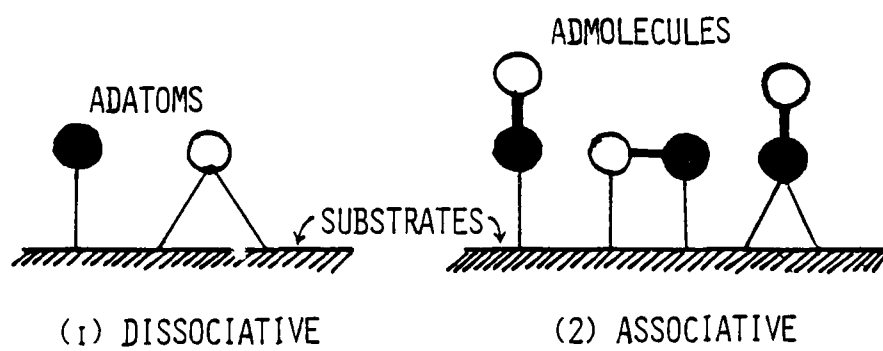
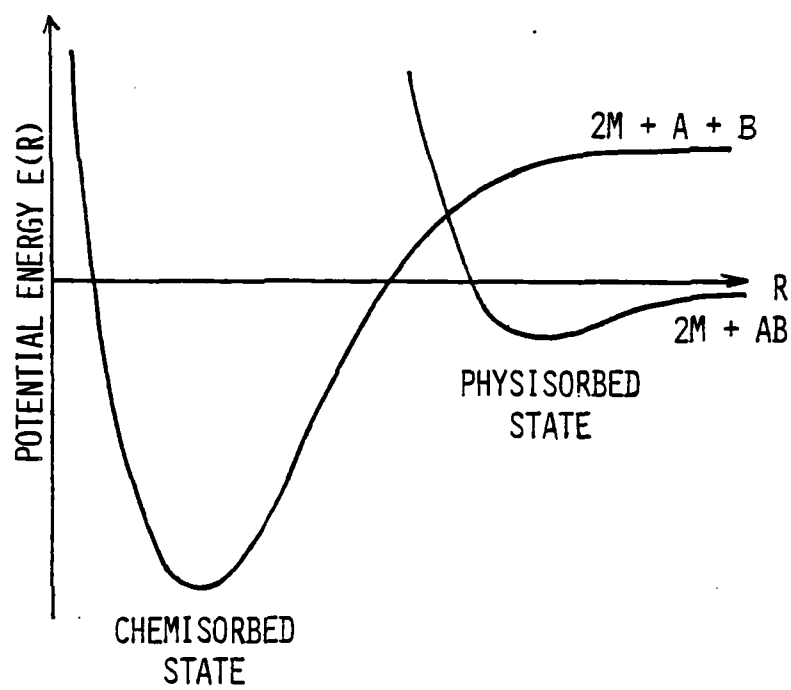
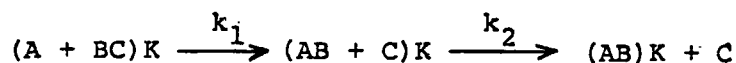


FIGURE 9

The reaction rates k_1 and k_{-1} might be comparable due to the unstable complex $((ABK))$. The k_2 reaction path therefore involves the stabilization of the complex $((ABK))$ by the removal of the excess energy. By means of laser radiation, one can either de-excite the $((ABK))$ complex and remove the excess energy assisted by the surface phonon modes, or selectively break the B-K bond and hence accelerate the k_2 rate to form the stable combined molecule (AB).

Consider now a typical reaction process on catalyst surface (K):



This involves bond breaking in B-C (k_1 path) and C-K (k_2 path). If one could enhance this bond breaking with resonant laser radiation, the overall reaction rate might be significantly enhanced.

(2) Laser-Enhanced Selective Migration and Applications to VLSI

One of the important industrial applications of LSSP is in the area of "very large scale integrated circuits" (VLSI), where the primary processes of the fabrication of a modern microelectronic circuit, such as chemical vapor deposition (CVD) and the growth rate of a deposited thin film, can be controlled (or assisted) by laser radiation.³⁴

For a simple example showing laser-enhanced selective

migration and laser-assisted CVD, let us consider the situation illustrated in Fig.10.

The x and y axes represent directions on the crystal surface along which the intrinsic barriers for migration, E_x^A and E_y^A respectively, are different ($E_x^A > E_y^A$). If a laser with photon energy E_0 is incident on the surface so that the active mode associated with the adsorbed species is pumped at a rate V , our model gives a transition rate for migration from one site to the next along the x and y directions in the Arrhenius-like form⁸

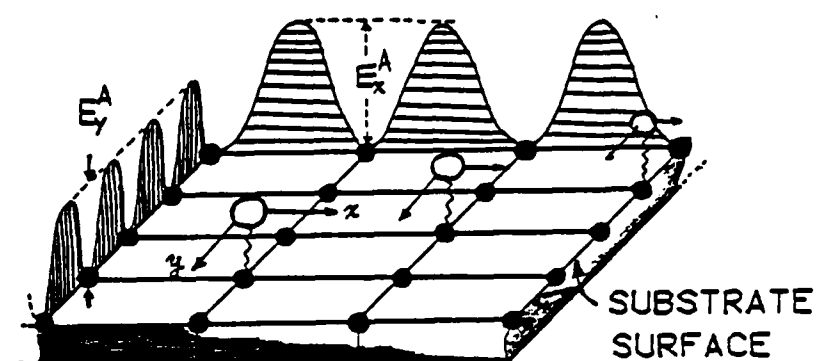
$$W_x = v_x \left(\frac{g_x V}{g_x^2 + V^2} \right)^2 \exp [-(E_x^A - E_0)/k_B T], \quad (3.33)$$

$$W_y = v_y \left(\frac{g_y V}{g_y^2 + V^2} \right)^2 \exp [-(E_y^A - E_0)/k_B T]. \quad (3.34)$$

Here $v_x(v_y)$ is the jumping frequency in the x(y) direction, g_x and g_y are the corresponding coupling factors of the bending (migration) modes with the active (stretching) mode, k_B is the Boltzmann constant and T the surface temperature. These rate equations provide us with criteria for selectively enhancing the mobility in the y direction, associated with the control of diffusion-limited rate processes. While this is the primary application of the migration model, increased migration can also result in enhanced desorption (or, alternatively, enhanced deposition) probabilities, with appropriate control applications in CVD.

Figure 10. Schematic diagram of adspecies chemisorbed on a solid surface with different migrational energy barriers E_A^x and E_A^y .

LASER-ENHANCED SELECTIVE MIGRATION



○ CHEMISORBED SPECIES

● SURFACE ATOMS

E_x^A AND E_y^A ARE THE MIGRATION BARRIER ENERGIES IN THE X AND Y DIRECTIONS.

$$W = \nu \left[\frac{g \cdot V}{g^2 \cdot V^2} \right]^2 e^{-(E^A - E_0)/kT_s}$$

* J. Lin and T. F. George, J. Phys. Chem. 84, October(1980)

FIGURE 10

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